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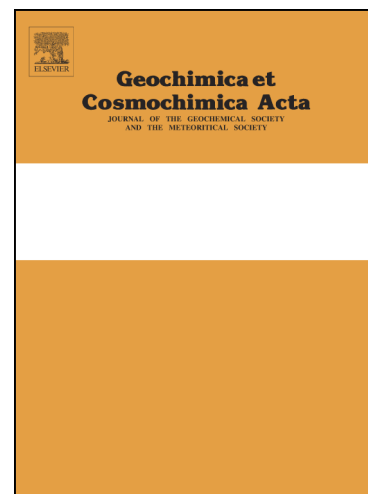
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Rapid Organic Matter Sulfurization in Sinking Particles from the Cariaco Basin Water Column

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Abstract

Organic matter (OM) burial in marine sediments is a potentially important control on global climate and the long-term redox state of the earth's surface. Still, we have only a limited understanding of the processes that stabilize OM and facilitate its preservation in the geologic record. Abiotic reactions with (poly)sulfides can enhance the preservation potential of OM, but for this process to be significant it needs to compete with OM remineralization, the majority of which occurs before sinking particles reach the sea floor. Here we investigate whether OM sulfurization occurs within sinking particles in the Cariaco Basin, a modern sulfidic marine environment with high rates of OM burial. Proto-kerogen in sinking particles is frequently more sulfur-rich and ³⁴S-depleted than expectations for biomass, with a composition that is difficult to explain by mixing with resuspended or terrigenous material. Instead, it appears that sulfur is being incorporated into OM on a timescale of days in sinking particles. The flux of this abiogenic organic S from particles is equivalent to approximately two-thirds of the total amount of proto-kerogen S at 10 cm depth in underlying sediments (ODP Core 1002B); after 6000 years of more gradual sulfurization reactions, potential water column sources are still equivalent to nearly half of the total proto-kerogen S in Cariaco sediments. Water column sulfurization is most extensive during periods of upwelling and high primary productivity

and appears to involve elemental S, possibly via polysulfides. This process has the potential to deliver large amounts of OM to the sediments by making it less available for remineralization, generating OM-rich deposits. It represents a potentially dynamic sink in the global carbon cycle that can respond to changes in environmental conditions, including the size and intensity of O₂-depleted environments. Water column OM sulfurization could also have played a more significant role in the carbon cycle during ocean anoxic events, for example during the Cretaceous.

1. Introduction

Only a small fraction of organic matter (OM) produced in the surface ocean escapes remineralization and is buried in marine sediments. Under certain conditions, however, large amounts of OM can be preserved in sediments and enter the long-term carbon cycle, potentially driving major changes in global climate and forming important petroleum source-rocks. OM-rich sediments are commonly associated with sub-oxic or anoxic conditions (Canfield, 1989; Emerson and Hedges, 1988; Hartnett et al., 1998), but the details of the relationship between O₂ availability and OM preservation have been contentious for decades. As the OM produced in the photic zone of the ocean sinks, it is both degraded and transformed (Fig. 1). Especially following plankton blooms, OM can agglomerate and combine with other biogenic material into macro-aggregates that sink to the seafloor within hours to days while some proportion of the OM they contain is remineralized by heterotrophic microorganisms. The sinking flux of OM is less attenuated with depth when O₂ concentrations in the water column are low (Devol and Hartnett, 2001; Keil et al., 2015), and OM is generally more resistant to microbial

degradation under anoxic conditions (Harvey et al., 1995; Hulthe et al., 1998). This effect, however, is apparently not due to slower rates of heterotrophic metabolism under anoxic conditions. Previous work suggested that it may instead reflect differences in the accessibility of certain classes of OM to anaerobic microorganisms or their metabolic demands (Lee, 1992; Van Mooy et al., 2002).

Organic matter sinking through the water column is consumed by microorganisms using a variety of electron acceptors (Fig. 1), generating both dissolved inorganic carbon and small organic molecules. This reactive organic material can subsequently undergo abiotic condensation and polymerization reactions to generate stable, macromolecular, amorphous material called kerogen (Vandenbrouke and Largeau, 2007). Special condensation reactions can occur in the presence of sulfide (e.g., Sinninghe Damsté et al., 1988; Kohnen et al., 1991) in which sulfur is added to OM by reaction with functionalized organic compounds, generating ‘abiogenic organic S.’ The resulting sulfur-rich OM is relatively resistant to biodegradation (Boussafir et al., 1995; Sinninghe Damsté and De Leeuw, 1990), making OM sulfurization a potential mechanism for enhancing OM preservation. Still, the timescale of this process – i.e., whether it occurs within sinking particles, versus solely in sediments – remains unclear.

The literature includes examples of sulfurization occurring over thousands of years of sediment diagenesis (e.g., Eglinton et al., 1994) as well as immediately near the sediment surface (e.g., Francois, 1987). Sulfurized OM is commonly observed in very shallow sediments, suggesting rapid formation in the uppermost parts of euxinic environments

(Bruchert and Pratt, 1996; Putschew et al., 1996; Werne et al., 2003; Wakeham et al., 1995) or even within anoxic microzones above the H_2S – O_2 interface (Francois, 1987). Li et al. (2011) found elevated concentrations of organic sulfur in suspended particles near the chemocline in the Cariaco Basin water column and proposed that this indicated early OM sulfurization. Rapid OM sulfurization in particles sinking through the water column was also proposed to explain the high S:C ratios in certain OM-rich rocks (van Dongen et al., 2006; Tribovillard et al., 2004). Support for the feasibility of more rapid OM sulfurization is also provided by laboratory experiments. In the presence of phase transfer catalysts and at moderate temperature, kerogen-like polymers and organic sulfur (OS) compounds have been generated from reactions with dissolved polysulfides within weeks (Rowland et al., 1993; Krein and Aizenshtat, 1994; Gelin et al., 1998; Kok et al., 2000; van Dongen et al., 2003). Similar products can form with similar mechanisms and rates under environmental temperatures and without catalysis (Amrani and Aizenshtat, 2004a). Rapid OM sulfurization could thus substantially enhance the stabilization and burial of OM in anoxic environments. Nevertheless, there is little direct evidence for this process in the modern ocean.

Complicating matters, OM sulfurization in modern, early diagenetic sediments is often described as a process occurring on timescales of hundreds to thousands of years rather than days. The sulfur content of OM increases steadily with depth below the sediment-water interface in Cariaco Basin (Werne et al., 2003, Aycard et al., 2003) as well as Jervis Inlet (Francois, 1987) and the Peru margin (Eglinton et al., 1994), which is thought to reflect gradual, kyr-scale sulfurization. Some lipid-derived organosulfur compounds

(OSC) also appear to form on this timescale (Werne et al., 2000; Sinninghe Damsté et al., 2007; Raven et al., 2015). Currently, we have few constraints on the quantitative importance of gradual versus rapid sulfurization reactions or their significance for proto-kerogen formation in marine sediments.

In this study, we approach these questions by interrogating the distribution of sulfur and its isotopic composition in sediment trap material from Cariaco Basin in the context of hydrographic profiles and particle composition time-series data (Thunell et al., 2000; <http://imars.marine.usf.edu/CAR/>). These μg -scale analyses are made possible via the novel use of multicollector inductively-coupled-plasma mass spectrometry to analyze bulk organic fractions (Raven et al., 2016). Sulfide is present in the Cariaco Basin water column below approximately 250 m depth, and underlying sediments are rich in organic C (~4 wt%) and organic S (~0.3 wt%). We present concentrations and $\delta^{34}\text{S}$ values for various pools of organic and elemental sulfur in particles, including individual organosulfur compounds. The results indicate that OM sulfurization does occur in the Cariaco water column following phytoplankton blooms and permit us to make the first quantitative estimates of the significance of water column sulfurization for OM burial in sediments.

2. Methods

2.1 Study site

Cariaco Basin, located off the north coast of Venezuela, has restricted circulation and becomes sulfidic below its chemocline at approximately 250 m depth (Li et al., 2010, Fig.

1). Seasonal, wind-driven upwelling events fuel strong phytoplankton blooms in the photic zone. As the organic products of these blooms sink, they are remineralized at rates comparable to those from the oxic open ocean and even higher near the chemocline (Muller-Karger et al., 2001). Nevertheless, about 10 g/m²/yr organic carbon escapes remineralization in the water column and is delivered to underlying sediments. A time-series study was initiated in Cariaco Basin in 1995 (Muller-Karger et al., 2001) and utilizes a set of automated sediment traps positioned at various depths in the water column (Fig. 1). Trap Z (150 m) is located in water with ~100 μM O₂; Trap A (at 225 m) is typically just above the chemocline, where <10 μM O₂ was recently measured (Li et al., 2011); and Traps B, C, and D (at 400, 880, and 1200 m depth, respectively) are bathed in >20 μM sulfide. Each cone-shaped trap collects sinking particles within a 0.5 m² area during 13 sequential two-week-long periods and preserves them with a formalin solution. The sediment trap mooring is recovered and re-deployed every six months. Samples have been stored frozen since collection.

Our samples represent splits of the trap material collected during 12, two-week periods between May 1999 and February 2010. For each collection period, we use samples from three or more traps to document depth-related patterns. An initial round of investigation focused on individual sulfur-bearing compounds, and the scope of work was subsequently expanded to include bulk extractable organosulfur fractions and proto-kerogen. Sediment trap samples are compared with previously published data from ODP Core 1002B, primarily Raven et al. (2015), Lyons et al. (2003), and Werne et al. (2003).

The core was collected in a shallower part of the basin (900 m water depth, Fig. 2) than the sediment trap mooring.

2.2 Sample Preparation and Analysis

Samples were freeze-dried and microwave-extracted twice into 9:1 dichloromethane (DCM):methanol (MeOH) at 100° for 15 minutes (MARS 5, CEM Corp). Extracts were separated by silica gel chromatography into non-polar (f1, 4:1 hexane:DCM), intermediate polarity (f2, DCM), and polar (f3, 1:1 DCM:MeOH) fractions. Extractable material that was immiscible in 4:1 hexane:DCM – similar to an asphaltene fraction from a mature deposit – was termed ‘strongly polar’ (f4). Each fraction was split into aliquots for compound-specific and bulk analysis. Elemental sulfur was removed from the non-polar fraction by exposure to activated Cu (Blumer, 1957), after which an additional aliquot was taken for bulk analysis of non-polar S_{org} (below). Solvent-extracted sediments were washed with Milli-Q water and leached with 1 M nitric acid at 20° C for ten days (Schimmelmann and Kastner, 1993) to oxidize pyrite and hydrolysable organic matter. We refer to the remaining material, which is not soluble in organic solvent, water, or nitric acid, as ‘proto-kerogen’ for consistency with Raven et al. (2015). Carbon and sulfur in proto-kerogen and $\delta^{34}S$ values were measured by combustion elemental analysis – isotope ratio mass spectrometry (EA-IRMS). Typical analytical uncertainties based on standard replicates were $\pm 2.5\%$ for concentrations and $\pm 0.5\%$ for $\delta^{34}S$ values. In-house measurements of carbon concentration were used whenever possible; the only significant difference between our dataset and published organic carbon contents

(<http://imars.marine.usf.edu/CAR/>) is for materials from February 2010, when our carbon concentration data are 30–60% higher.

Aliquots for bulk analysis were dried and oxidized in 30% H_2O_2 (reagent grade) at 90° for 24 hours in glass vials with teflon-coated septa. Sulfate was separated from other ions on AG1-X8 anionic exchange resin (Paris et al., 2013). Resin was washed with ten column volumes (CV) 10% HNO_3^- , conditioned with 10 CV 10% HCl and 10 CV 0.5% HCl , loaded in .05% HCl , and washed with 3 x 5 CV H_2O before sulfate was eluted in 0.5N HNO_3 . Sulfate samples were stored dry in Teflon vials until analysis. The sulfur content of each OS fraction was measured as sulfate by ion chromatography (IC, Dionex ICS-2000) with an AS-19 anion column and AERS 500 ion regeneration. Concentrations were used to intensity-match samples and the required Na^+ supplement for analysis using a Thermo Neptune⁺ multicollector inductively coupled plasma mass spectrometer (ICP-MS) (Paris et al., 2013). Samples were injected into the plasma torch with a desolvating nebulizer (Aridus) and bracketed with known $\delta^{34}\text{S}$ NaSO_4 standards. The Neptune was operated in medium resolution ($M/\Delta M \sim 8000$) to resolve oxygen interferences on masses 32 and 34. Analytical precision for $\delta^{34}\text{S}$ was typically better than $\pm 0.2\text{‰}$.

Individual organic sulfur compounds within the non-polar and intermediate-polarity fractions were initially investigated with a Varian CP-3800 gas chromatograph (GC) coupled in parallel to a mass spectrometer (MS, Varian Saturn 2200 ion trap) and a sulfur chemiluminescence detector (SCD, Sievers 355). When possible, compounds were identified by their EI mass spectra. The abundance of individual compounds was

calculated relative to an internal standard. Subsequently, compound-specific sulfur-isotopic measurements were made using the system originally described in Amrani et al. (2009) as modified by Raven et al. (2015). An Agilent 6890 GC was coupled via a custom-built heated transfer line to the plasma torch of the Neptune⁺ ICPMS operated in medium resolution. Isotope ratios were standardized to a gas-phase standard (SF₆) that can be injected as either discrete peaks or a continuous flow for machine tuning. The argon ‘sample gas’ constituting the core of the plasma was preheated to 320° prior to meeting the GC helium carrier gas effluent at the downstream end of the 320° transfer line. This system is capable of obtaining accurate and precise (typically better than $\pm 1.0\%$) $\delta^{34}\text{S}$ values for as little as 100 picomoles of sulfur in an individual, volatile compound. Uncertainties improved to approximately $\pm 0.3\%$ for larger, well-resolved chromatographic peaks. Data were exported from the Neptune software to Isodat 3.0 for integration and processing.

3. Results

3.1 Carbon and sulfur in particulate proto-kerogen

Tables 1 and 2 present results for 26 sediment trap samples collected on seven dates between 2006 and 2010, including five consecutive periods in Winter 2007. Mass flux data in Table 1 are from <http://imars.marine.usf.edu/CAR/>. The fluxes of organic carbon and sulfur in proto-kerogen average 5.2 mmol C/m²/d and 105 $\mu\text{mol S/m}^2\text{/d}$ (Table 1), and particles have an average molar S:C ratio of 1.9% (ranging from 0.6% to 3.8%). About fifty-fold less organic S is present in the extractable fractions (Table 2) than in proto-kerogen. The largest fluxes of extractable organic S are for material in the polar

fraction (f3, averaging $1.6 \mu\text{mol S/m}^2/\text{d}$), followed by the strongly polar (f4, $0.39 \mu\text{mol S/m}^2/\text{d}$) and non-polar (f1, $0.12 \mu\text{mol S/m}^2/\text{d}$) fractions. The intermediate polarity extractable OS fraction ($0.24 \mu\text{mol S/m}^2/\text{d}$) potentially includes the products of reactions between the trap preservative (formaldehyde) and dissolved sulfide, so we do not discuss it further here. Fluxes of elemental sulfur (S^0) average $0.8 \mu\text{mol S/m}^2/\text{d}$ and range from 0.0 to $4.7 \mu\text{mol S/m}^2/\text{d}$.

The $\delta^{34}\text{S}$ values observed for S^0 , two individual OS compounds, extractable OS fractions, and proto-kerogen are summarized in Figure 3. All of our $\delta^{34}\text{S}$ results fall below seawater sulfate $\delta^{34}\text{S}$ ($\sim 21.1\text{‰}$) and that expected for biosulfur. All of the extractable and proto-kerogen OS pools have overlapping $\delta^{34}\text{S}$ ranges between 0 and 20‰ , with average isotopic compositions of 8.3, 7.0, and 8.7‰ for the non-polar, polar, and strongly polar extractable OS fractions, respectively. Proto-kerogen is somewhat less ^{34}S -depleted on average (12.7‰) than the extractable OS fractions. None of these values match expectations for marine assimilatory biosulfur ($18\text{--}22\text{‰}$, Kaplan and Rittenberg, 1964), although individual proto-kerogen and S^0 measurements approach biosulfur-like values on some dates. The isotopic composition of S^0 ranges from -5.9 to 10.8‰ in traps below the chemocline, and reaches 18.9‰ in our 250 m sample from March 2007.

3.2 Compound-specific $\delta^{34}\text{S}$ results

Two isomers of a C_{20} isoprenoid thiophene, interpreted as the sulfurized products of phytol, are consistently observed in sediment trap extracts. These compounds match the retention times and EI mass spectra reported for C_{20} isoprenoid thiophenes in Cariaco

sediments (Raven et al., 2015) and prior published mass spectra (Brassell et al., 1986; Putschew et al., 1996). The results presented here for ‘C₂₀ thiophene’ are for the more abundant, earlier-eluting isomer. At concentrations of up to 5.3 nmol S/g, C₂₀ thiophene represents less than 1% of the non-polar extractable organic S fraction. High C₂₀ isoprenoid fluxes in winter 2007 are associated with a dramatic shift toward more ³⁴S-enriched compositions relative to other investigated dates. C₂₀ thiophene $\delta^{34}\text{S}$ values for March 2007 and February 2010, for example, differ by nearly 30‰. The most ³⁴S-depleted C₂₀ thiophenes have $\delta^{34}\text{S}$ values near -30‰, similar to observations of dissolved sulfide in the Cariaco water column (Li et al., 2010).

We are also able to measure $\delta^{34}\text{S}$ values for the most abundant GC-amenable organosulfur compound in the intermediate-polarity fraction of 8 samples (Table 2). We previously encountered the same compound in ODP Core 1002B, collected nearby in the basin, and refer to it as “U-14” for consistency with Raven et al. (2015). Nevertheless, attempts to identify this compound are frustrated by its very low concentration relative to other, coeluting compounds, and it can not be measured in samples from winter 2007 because the intermediate-polarity fraction is extremely rich in non-sulfur bearing compounds. Measured $\delta^{34}\text{S}$ values for U-14 range from -33 to -8‰.

4. Discussion

4.1 Proto-kerogen sulfur in sinking particles

Sinking organic matter in Cariaco Basin is primarily the product of phytoplankton productivity in the surface ocean (Thunell et al., 2000) and contains biosulfur

predominantly as cysteine and methionine. The ratio of sulfur to carbon in fresh planktonic biomass is commonly estimated at 1.6% (Wollast et al., 1993) but was also found to range between 0.4% and 1.1% in a variety of diatoms, dinoflagellates, cyanobacteria, algae, and humic acids (Francois et al., 1987 and refs therein). Biosulfur derives from the assimilation of seawater sulfate, which has a $\delta^{34}\text{S}$ value of 21.2‰ in the Cariaco Basin (Li et al., 2010). Assimilatory sulfate reduction exhibits very little S-isotope fractionation, so fresh biomass is expected to have a $\delta^{34}\text{S}$ value between about 18 and 21.2‰ (Kaplan and Rittenberg, 1964). These ranges for the S:C ratio and $\delta^{34}\text{S}$ value of fresh biomass are compared with OM from sediment traps in Fig. 4.

The sulfur isotopic composition of particulate proto-kerogen is more ^{34}S -depleted than the range of anticipated biosulfur in all of our samples (Fig. 4), and we find coherent patterns in $\delta^{34}\text{S}$ values by date. The most biosulfur-like $\delta^{34}\text{S}$ values for proto-kerogen (up to 17.9‰) are observed in February 2010 and above the chemocline in October 2006, while proto-kerogen is more strongly ^{34}S -depleted below the chemocline in October 2006 and throughout winter 2007. S:C ratios of proto-kerogen are substantially higher than biomass during three of the five sampling periods in winter 2007 and in 'C' trap in February 2010. Proto-kerogen S:C ratios are in some cases more than twice those of fresh algal biomass, reaching 3.8% (Fig. 4). The average S:C ratio in Cariaco particles, 1.9%, is similar to ratios reported for a variety of OM-rich sediments, including the Cariaco Basin (mean 2.4% in the upper 100 cm, Werne et al., 2003), the Kimmeridge Clay ($\leq 6\%$, mean 2.5%, Van Kaam-Peters et al., 1998), the Peru Margin (1.1% – 5.6%, Mossman et al., 1991), a salt marsh in Delaware, USA (~5% in base-extractable humic material,

Ferdelman et al., 1991), and Jervis Inlet (1.1 to 1.9%, Francois, 1987). Comparable ratios were also found in particles from the Philippine Sea (Chen et al., 1996, Fig. 5). Lower S:C ratios were reported for sediments with variable OM contents off the coast of California (0.6 to 1.5%, Nissenbaum and Kaplan 1972). Although the position of the chemocline varies among these environments, their S:C ratios are reminiscent of those from sinking particles in Cariaco Basin, suggesting that rapid sulfurization – in particles, shallow sediments, or sulfidic microenvironments – may be important for OM preservation in diverse environments.

The S:C ratios and $\delta^{34}\text{S}$ values of particulate proto-kerogen samples are plotted in Fig. 5. Fresh biomass that sinks out of the photic zone of the ocean will undergo heterotrophic degradation, condensation reactions, and mixing with other materials (Eglinton et al., 1994), each of which will change the S:C ratio and $\delta^{34}\text{S}$ value of proto-kerogen in different but predictable ways. OM degradation is likely to decrease the S:C ratio of proto-kerogen, especially if proteins (the main biochemical reservoir for sulfur) are preferentially remineralized relative to carbohydrates and lipids. Proteins are preferentially remineralized in the sub-oxic water column of the eastern tropical North Pacific (Van Mooy et al., 2002) but degrade at similar rates to carbohydrates and proteins in oxic and anoxic incubations (Harvey et al., 1995). S:C ratios below those of biomass were reported in sinking and suspended particles in oxic water off the California coast (S:C = 0.84% and 0.45%, respectively) and were attributed to the preferential remineralization of S-bearing proteins by heterotrophic microorganisms (Matrai et al., 1989). Similarly, the proto-kerogen S:C ratios below ~1.0% that we observe in a few

samples likely reflect the heterotrophic degradation of protein-rich OM. Heterotrophy has likely influenced the S:C ratio of all of the particle samples to some extent, but it should not cause fractionation in the S isotopes of OM (vertical dashed arrows, Fig. 5).

Heterotrophy cannot, however, explain the fact that proto-kerogen is often more sulfur-rich and ^{34}S -depleted than planktonic or degraded biomass. Other potentially important processes in the Cariaco water column include mixing with terrigenous or resuspended detrital material and condensation reactions, particularly OM sulfurization. The effect of resuspension is shown on Fig. 5 as a mixing field between biomass and proto-kerogen in surface sediments from Cariaco Basin (upper 100 cm of ODP Core 1002B sediments, Werne et al., 2003). Similarly, mixing with an estimated terrigenous end-member can decrease particle proto-kerogen $\delta^{34}\text{S}$ values but fails to explain S:C ratios above about 2%. S:C ratios can be increased by OM sulfurization, which as a broad generalization adds sulfur to proto-kerogen by replacing oxygen atoms without removing carbon. The isotopic composition of the sulfur that could be added is only weakly constrained, so the vectors representing OM sulfurization on Fig. 5 indicate a range of effects for incorporating sulfur with a $\delta^{34}\text{S}$ value between -30‰ and 10‰. Two other processes have the potential to influence proto-kerogen characteristics but are set aside in the following discussion due to a lack of available data: the hypothesized assimilation of reduced sulfur species into biomass (e.g., Canfield, 1998) and the potential for natural marine biomass to differ substantially from the limited literature data for particle S:C and $\delta^{34}\text{S}$ due to other environmental sensitivities.

Nearly all of the proto-kerogen S:C and $\delta^{34}\text{S}$ data for Cariaco particles can be explained by a combination of heterotrophy, resuspension, and sulfurization. Samples from three consecutive sampling periods in winter 2007 fall within the ‘S-addition’ field, which is best explained by the chemical addition of sulfur to OM (Fig. 5). Results from October 2006, on the other hand, are most consistent with mixing with terrigenous or resuspended material. For the remaining samples, including those from February 2010 and parts of winter 2007, proto-kerogen $\delta^{34}\text{S}$ values and S:C ratios could result from either mixing with detrital material or a combination of OM sulfurization and heterotrophy; combinations of these processes are likely important. In the following section, we explore what environmental conditions might have supported these different patterns using oceanographic and geochemical data from the CARIACO database (<http://imars.marine.usf.edu/CAR/>).

4.2 Hydrography and primary productivity during sampling

Water column profiles of potential density (σ_θ) and chlorophyll-*a* from the CARIACO time-series program for the three-month period surrounding each of our main sampling dates are shown in Fig. 6. A well-mixed water column persisted for at least two months in winter 2007, driving high productivity (chlorophyll *a*) in early February and lower productivity in March. Dates on which particulate proto-kerogen samples fall in the ‘S-addition’ field of Fig. 5 were thus broadly characterized by strong upwelling and high productivity in the surface ocean. In contrast, the water column in October 2006 was strongly stratified in the upper 200 m. There was also some upwelling in February 2010,

but it appears to have been less intense, with a brief, strong bloom at the start of the sampling period and restratification by early March.

We next place these dates in the broader context of particle composition throughout the time-series (<http://imars.marine.usf.edu/CAR/>). ‘Z’ trap in winter 2007 contains very little terrigenous material and abundant OM, consistent with the indicators of high primary productivity at this time (Fig. 7). Relative to the rest of the seven-year time-series, winter 2007 stands out in terms of both terrestrial material and organic C flux. Fluxes of OM were unremarkable in deeper traps during winter 2007, indicating that OM remineralization during sinking was extensive; however, the remaining OM frequently falls within the ‘S-addition’ field of Fig. 5. Unlike winter 2007, the February 2010 and October 2006 sampling periods are similar to long-term averages in terms of both terrigenous material and organic C flux. Their differences appear to largely reflect seasonal variability, with bloom-season particles from February 2010 transporting more organic C and a lower proportion of terrestrial material than those collected during the rainy season, in October 2006. Overall, the extent of OM sulfurization appears to correlate with bloom intensity and export production, making its effects on proto-kerogen composition particularly apparent during the intense upwelling and TOC export of winter 2007. More typical upwelling periods like February 2010 may also facilitate OM sulfurization in particles, but to a lesser extent.

4.3 Correlated $\delta^{34}\text{S}$ variability in winter 2007

In addition to proto-kerogen, we measured the concentrations and $\delta^{34}\text{S}$ values of elemental S and the most abundant non-polar organosulfur compound extracted from trap materials, C_{20} thiophene (Table 3 and Fig. 8). S^0 and C_{20} thiophene are generally abundant, ^{34}S -rich, and isotopically variable during winter 2007. Additionally, the $\delta^{34}\text{S}$ values of S^0 , C_{20} thiophene, and proto-kerogen are well correlated during winter 2007 but not with samples from other dates (Fig. 8). These patterns provide important clues about the likely mechanisms of OM sulfurization in particles.

Elemental S is central to current models for OM sulfurization because polysulfides (HS_n^- , S_n^{2-} , $n \leq 10$), which form spontaneously in the presence of dissolved sulfide and solid S^0 (Rickard and Luther, 2007), are thought to be the key reactive species in the formation of abiogenic organic sulfur (Kohnen et al., 1989; Vairavamurthy et al., 1992; Amrani and Aizenshtat, 2004b; Canfield et al., 1998; Mossman et al., 1991; Francois et al., 1987). The S_n^{2-} polysulfide species that are favored in S^0 -rich systems – predominantly S_4^{2-} , S_5^{2-} , and S_6^{2-} – derive half to two-thirds of their sulfur atoms from elemental sulfur and the remainder from sulfide (Kamyshny et al., 2004; Amrani and Aizenshtat, 2004b). Polysulfide $\delta^{34}\text{S}$ values should therefore reflect mixing between particulate S^0 and water column bisulfide, which has a $\delta^{34}\text{S}$ value that is consistently near -30‰ (Li et al., 2010).

A genetic link between polysulfides and sulfurized OM during winter 2007 is evidenced by the strong correlations between S^0 $\delta^{34}\text{S}$ values and those of both proto-kerogen and C_{20} thiophene (Fig. 8), with R^2 values of 0.69 and 0.88, respectively. The slope of the regression line for S^0 and C_{20} thiophene $\delta^{34}\text{S}$ values is approximately 0.6, which would be

consistent with C₂₀ thiophene forming from a polysulfide pool derived from S⁰ and bisulfide in an average mixing ratio between 1:1 and 3:2. If we assume that polysulfides contain equal contributions of S atoms from bisulfide and from S⁰, we can estimate the isotope effect associated with C₂₀ thiophene formation. A line with a slope of 1.0 fit through the winter 2007 data has a y-intercept of ~7‰, implying an equilibrium-type isotope effect during the formation of C₂₀ thiophene from polysulfide of about 7‰. A similarly sized effect was observed in laboratory sulfurization experiments (4-5‰, Amrani and Aizenshtat, 2004b), although these prior experiments relied on bulk (ir-MS) rather than compound-specific analyses. Polysulfides are thus likely reactants for OM sulfurization in Cariaco particles during winter 2007.

4.4 Potential influence of mixing with terrigenous and resuspended sediment

Proto-kerogen, S⁰, and C₂₀ thiophene δ³⁴S data for February 2010 and October 2006 fall off of the winter 2007 trends (Fig. 8). In February 2010, relatively ³⁴S-enriched proto-kerogen δ³⁴S values could in part reflect dilution of abiogenic OS by large fluxes of unsulfurized biomass. However, detrital (terrigenous and resuspended) material is also a potentially significant source of OS to particles, especially in October 2006 and February 2010 (Fig. 5). In a study of pyrite (Cr-reducible S) in Cariaco sediment traps, Li et al. (2011) preferred to explain relatively ³⁴S-enriched (-6 to 1‰) pyrites and abundant S⁰ (27.3 μmol/g, 0.8 mg/g, trap Z) in some samples as being derived from resuspension of sedimentary pyrite and S⁰ formed elsewhere in the basin (Li et al., 2011). Resuspension is also a potential source of the ubiquitous, trace concentrations of ³⁴S-depleted C₂₀ thiophenes that we observe in deeper traps in October 2006, February 2010, and five

additional dates (-29.9‰ to -14.7‰, Table 3). These $\delta^{34}\text{S}$ values approach those measured in ODP Core 1002B (-37.1‰ at 40 cm depth, Raven et al., 2015). In contrast, resuspension does not appear to contribute significantly to particle OS in winter 2007, when C_{20} thiophene $\delta^{34}\text{S}$ values average -8.4‰ and proto-kerogen S:C ratios substantially exceed those measured in sediment (~2.0%).

Terrigenous material also appears to be a minor source of particle OS, despite the fact that terrigenous material accounts for about half of particle material in Cariaco Basin. The dominant sources of terrigenous material to Cariaco Basin throughout the year are local rivers, with some contribution from Saharan dust (Martinez et al., 2007). Both plant and animal terrestrial OM generally have lower $\delta^{34}\text{S}$ values than marine OM, although terrestrial OM $\delta^{34}\text{S}$ values will be largely controlled by rainwater sulfate and bedrock sulfur sources. The mixing line in Fig. 5 is based on $\delta^{34}\text{S}$ data for terrestrial OM from Bol et al. (2002), which ranged from 2 to 10‰; sulfate in rainwater falls in a similar $\delta^{34}\text{S}$ range. Because terrigenous detritus is relatively S-poor, it cannot explain the particulate S:C ratios we observe outside of October 2006. Moreover, several other geochemical proxies indicate that organic matter in Cariaco Basin particles is primarily marine rather than terrestrial in origin. Thunell et al. (2000) showed that the carbon isotopic compositions and N:C ratios of Cariaco Basin particles match expectations for marine phytoplankton ($\delta^{13}\text{C} = -20 \pm 2\text{‰}$, N:C = 16:106 = 14.7%) rather than terrestrial organic matter ($\delta^{13}\text{C} \leq -26\text{‰}$, N:C ~ 5%), and average values of $\delta^{13}\text{C}$ and N:C of Cariaco sediment trap samples have remained consistent through 2010 (<http://imars.marine.usf.edu/CAR/>). Biomarker studies of these sediment trap samples

also indicate that the majority of the sinking OM in Cariaco Basin is of marine origin (Goni et al., 2009).

4.5 Water column sources of organic S to sedimentary proto-kerogen

We next compare the delivery of sulfurized OM from the water column to OM preservation in Cariaco sediments (ODP Core 1002B). Sediment proto-kerogen $\delta^{13}\text{C}$ values (-20 to -18‰, Fry et al., 1991) are a good match for particles, suggesting that this OM should be derived from the water column. Proto-kerogen sulfur, however, is much more ^{34}S -depleted in sediments than in sinking particles. In both environments, proto-kerogen $\delta^{34}\text{S}$ values can be thought of as a mixture of primary productivity-derived biosulfur with a $\delta^{34}\text{S}$ value near 20‰ and a pool of abiogenic OS with a more ^{34}S -depleted isotopic composition (Eglinton et al., 1994; Anderson and Pratt, 1995). The $\delta^{34}\text{S}$ value of this abiogenic OS end member probably varies, reflecting the dynamic S-isotopic composition of S^0 in particles. We therefore select two bounding values for abiogenic OS to constrain the potential size of the abiogenic OS flux (Table 4): a $\delta^{34}\text{S}$ value of -30‰ matches sulfide in the deep Cariaco water column (Li et al., 2011), while a $\delta^{34}\text{S}$ value of 5‰ represents the sulfide that would be generated by dissimilatory sulfate reduction in the water column with a moderate isotope fractionation factor (ϵ) of -15‰. The implied fluxes of ^{34}S -depleted abiogenic OS are converted to equivalent sedimentary concentrations based on an estimated average mass accumulation rate of $\sim 13.2 \text{ g/m}^2/\text{yr}$ (Lin et al., 1997; Shipboard Scientific Party, 1997). We use the concentration of proto-kerogen S at 10 cm depth in Cariaco Basin sediments, $95 \text{ } \mu\text{mol S/g}$, as an estimate of the total accumulation of abiogenic OS from the water column and shallow (0–10 cm)

sedimentary processes (Raven et al., 2015; Aycard et al., 2003). Subsets of these results are averaged in Table 4 to explore the significance of depth and water column conditions on abiogenic OS flux.

The implied source of abiogenic OS from the water column based on a simple average of the available data is 46 $\mu\text{mol/g}$. A more realistic estimate may be the average of only data from C trap, which is located at 880 m and is most equivalent to delivery at the ODP 1002B core site (900 m). (Lower fluxes of OS as well as total particle mass in D trap are consistent with the long-term dataset and may be circulation and/or bathymetry-related, see Fig. 1 and Table 1). The potential abiogenic OS accumulation based on C trap results (65 $\mu\text{mol/m}^2/\text{d}$) is equivalent to 68% of proto-kerogen S at 10 cm depth in the sediments (Fig. 9). This value, which assumes an abiogenic OS $\delta^{34}\text{S}$ value of -30‰, is a minimum estimate of the actual source. Data from February 10, 2010 and the 225 m trap on March 14, 2007 suggest that abiogenic OS may have a $\delta^{34}\text{S}$ value closer to 5‰ (Fig. 5), which would imply a larger water column source that could even exceed sedimentary concentrations (Table 4).

Below 10 cm depth in Cariaco Basin sediments, OS concentrations gradually increase by about 50% to ~150 $\mu\text{mol/g}$. Sedimentary sulfurization on this timescale (approximately 6000 years) in Cariaco Basin was described in Aycard et al. (2003) for proto-kerogen and by Werne et al. (2008) and Raven et al. (2015) for individual extractable organic compounds. Similar patterns have been found in Peru Margin sediments and elsewhere (Eglinton, 1994). However, only about one-third of the sulfur in deeper (3 m) Cariaco

sediments appears to derive from these slower, diagenetic reactions. By our estimates, slightly less than half of that proto-kerogen S is delivered from the water column, with processes within the uppermost 10 cm of the sediments accounting for the remainder.

4.6 Significance of rapid OM sulfurization for carbon burial

The quantitative significance of water column-derived, abiogenic OS will depend on the frequency of periods like winter 2007, when environmental conditions appear to have been particularly conducive to the production of abiogenic OS in the water column. Given our two-week sampling resolution, it is challenging to make more specific correlations between abiotic OS fluxes and nimble processes like phytoplankton blooms. OM export fluxes in Cariaco Basin particles have been shown to respond to surface productivity on timescales of days to weeks (Montes et al., 2012). Similarly, sulfurization intensity appears to respond dynamically to changes in circulation and surface productivity. Previous studies have found evidence for rapid OM sulfurization in a variety of environments (Sinninghe Damsté et al. 2007; Wakeham et al. 1995; Hartgers et al., 1997; Putschew et al., 1996; Canfield et al., 1998; Francois et al., 1987; Mossman et al., 1991), but it has been challenging to understand sulfurization rates near the sediment-water interface using annual-scale archives like sediments and rocks. The higher resolution record offered by sinking particles demonstrates that OM sulfurization can occur within days or less.

The vast majority of OM exported from the surface ocean is remineralized before reaching the underlying sediments. Sulfurization of OM within particles can therefore

affect a much larger pool of OM than sulfurization in sediments alone. Under the right conditions, water column sulfurization could compete with remineralization for labile OM and enhance the likelihood of OM preservation in underlying sediments (Sinninghe Damsté et al., 1989; Boussafir et al., 1995). Our results thus support the conclusions of van Dongen et al. (2006) and others, who hypothesized that rapid carbohydrate sulfurization in a euxinic water column could explain the extremely high concentrations of sulfur-rich OM in the Kimmeridge Clay (≤ 34 wt%) and other OM-rich rocks. Water column sulfurization could have played an expanded role in the carbon cycle during periods of expanded marine anoxia like the Cretaceous ocean anoxic events.

We also find some evidence that water column sulfurization may not be strictly limited to environments with measurable free sulfide in the water column. OM sulfurization was previously hypothesized to occur in micro-environments in sediments that were bathed in oxic porewater by Francois et al. (1987). The shallowest trap samples from two consecutive periods fall within the ‘S-addition’ field, despite being collected either just above the chemocline (A trap, 225 m) or substantially above it (Z trap, 150 m). The ‘A’ trap sample from March 14, 2007 is particularly notable, falling far out of the regions of Fig. 5 that can be explained by other sources. Additionally, this trap has very high fluxes of S^0 ($4.7 \mu\text{mol}/\text{m}^2/\text{d}$), polar extractable OS ($5.0 \mu\text{mol}/\text{m}^2/\text{d}$), and $1.3 \text{ nmol/g C}_{20}$ thiophene, all of which are consistent with the operation of an active S cycle. Polysulfides may exist at redox interfaces within OM-rich particles even in the presence of low concentrations of water column O_2 ($\leq 25 \mu\text{M}$, Ploug et al., 2001), as typically characterize A trap (Fig. 1, Li et al., 2010). If future work confirms the activity of OM sulfurization in

particles within sub-oxic ($\leq 25 \mu\text{M O}_2$) environments, it would greatly expand the potential significance of this process in the modern ocean to include many oxygen minimum zones. Rapid abiogenic organic S formation may also provide a mechanistic link between enhanced OM burial and environmental O_2 limitation (Hartnett et al., 1998; Devol and Hartnett, 2001) via the transformation of labile OM into more condensed, S-rich structures within sinking particles.

4.7 The S-isotope composition of rapidly sulfurized OM

The correlated S-isotopic compositions of S^0 , C_{20} thiophene, and proto-kerogen indicate that polysulfides are likely the main reactive species forming abiogenic organic S in the Cariaco water column. Polysulfides are in rapid isotopic equilibrium with S^0 and sulfide (Rickard and Luther, 2007; Amrani and Aizenshtat, 2004b), and a primary control on their $\delta^{34}\text{S}$ value is the isotopic fractionation associated with dissimilatory sulfate reduction. The scale of this fractionation varies with sulfate reduction rate and substrate availability, with faster metabolic rates and higher energetic yields generally producing smaller fractionations (e.g., Sim et al., 2011a; Leavitt et al., 2013). Given abundant sulfate in the water column, sulfate reduction rate should be primarily controlled by OM lability, which decreases with water depth. Accordingly, C_{20} thiophene $\delta^{34}\text{S}$ values, which appear to reflect the $\delta^{34}\text{S}$ value of polysulfide offset by a slight equilibrium-type isotope effect, decrease with trap depth (Fig. 8b). This pattern is consistent with increasing isotopic fractionations between sulfate and sulfide (and S^0) as OM is progressively consumed. The smallest apparent fractionation factors we observe are in the shallowest traps during the winter 2007 bloom, where high sulfate reduction rates are

particularly favored. On the other hand, large apparent fractionation factors for dissimilatory sulfate reduction (~50‰) are found in shallow Cariaco sediments, where the $\delta^{34}\text{S}$ value of porewater sulfide is approximately -29‰ (Werne et al., 2003) and individual organosulfur compounds have $\delta^{34}\text{S}$ values < -35‰ (Raven et al., 2015).

Like S^0 , the $\delta^{34}\text{S}$ value of abiogenic organic S from the water column is likely to vary widely on the timescale of blooms. Still, we can constrain its average $\delta^{34}\text{S}$ value more tightly than the bounding values explored above (-30‰ and 5‰) based on the $\delta^{34}\text{S}$ value of proto-kerogen at 10 cm depth (-21.2‰). The abiogenic organic S formed in the sediments, which appears to represent less than one-third of total proto-kerogen S at 10 cm depth, is relatively ^{34}S -depleted. Therefore the average $\delta^{34}\text{S}$ value of water column-derived abiogenic organic S must be somewhat more ^{34}S -enriched than -21.2‰ (roughly -20 to -5‰). This estimate is consistent with the weighted average delivery of C_{20} thiophene from the water column (-9.1‰) and typical fractionation factors for dissimilatory sulfate reduction in the environment (25 to 40‰, Habicht and Canfield, 2001; Sim et al., 2011b).

5. Conclusions

Particulate OM sinking through the water column of Cariaco Basin is often more sulfur-rich and ^{34}S -depleted than typical marine biomass, especially during a period of upwelling and high productivity in winter 2007. These results are best explained by the occurrence of abiogenic OM sulfurization in particles on timescales of days or less. Correlations among the $\delta^{34}\text{S}$ values of proto-kerogen, C_{20} thiophene, and S^0 suggest a genetic link between these species, likely via polysulfides. On dates outside of winter 2007, sediment resuspension and mixing with terrestrial detritus may be relatively important processes affecting particulate OS. Although the extent of water column sulfurization appears to vary with environmental conditions like primary productivity and OM export, we roughly estimate that water column sources can account for two-thirds of proto-kerogen S at 10 cm or slightly less than half of proto-kerogen S at 3 m depth in basin sediments. Rapid, abiotic OM sulfurization in sinking particles may represent a mechanistic link between O_2 -depleted environments and enhanced OM preservation in sediments.

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Figure 1. Cartoon of processes affecting sinking organic matter in the oxic and sulfidic parts of the Cariaco water column and underlying sediments. Dissolved oxygen and sulfide concentration profiles (left) are redrawn from Li et al. (2010). The species listed after ‘remineralization’ are the canonical electron acceptors for microbial heterotrophy in each zone. Sediment trap depths are shown at right.

Figure 2: Site Map. Bathymetry of Cariaco Basin, showing locations of traps and sediment core ODP 1002B.

Figure 3. Isotopic compositions of distinct sulfur pools in trap materials. Symbols represent average $\delta^{34}\text{S}$ values (‰, relative to VCDT) and error bars represent ranges for all dates and depths. The shaded gray bar at left spans the range of all previous observations of sulfide in the water column (Fry et al., 1991; Li et al., 2010). The shaded green bar at right spans expected $\delta^{34}\text{S}$ values of biosulfur (Kaplan and Rittenberg, 1964). U-14 is an unidentified organosulfur compound previously observed in Cariaco sediments.

Figure 4. $\delta^{34}\text{S}$ values and S:C ratios of proto-kerogen in trap materials. Data are from five periods in winter 2007 (triangles), February 2010 (open circles) and October 2006 (open squares). At left, the shaded region represents expected biosulfur $\delta^{34}\text{S}$ values (Kaplan and Rittenberg, 1964), and the heavy vertical line represents seawater sulfate $\delta^{34}\text{S}$. At right, the shaded region encompasses previously reported values of ‘typical’ S:C (mol/mol) ratios in particulates and the heavy vertical line represents the value for typical

algal biomass from Wollast et al. (1993). Depth profiles connected with lines fall within the ‘S-addition’ field discussed below. The dashed horizontal line in both panels shows the approximate position of the chemocline in Cariaco Basin. Hash marks at ~900 m on each panel indicate the total water depth at the location of ODP Core 1002B.

Figure 5. Processes influencing the $\delta^{34}\text{S}$ value and S:C ratio of proto-kerogen in particles. Symbols represent all available depths for five dates in winter 2007 (triangles), October 2006 (open squares), and February 2010 (open circles). The shaded green rectangle represents expected values for fresh algal biomass. Dashed vertical arrows indicate the effect of heterotrophic remineralization. Gray shaded fields represent the effects of mixing with resuspended or terrigenous material or the addition of abiogenic organic S with a $\delta^{34}\text{S}$ value between -30‰ and +10‰.

Figure 6: Density and chlorophyll-a concentrations in the Cariaco water column for three sample collection periods. The horizontal dashed line indicates the approximate position of the chemocline. Data are from the CARIACO time series (<http://imars.marine.usf.edu/CAR/>). The approximate depths of traps Z and A are shown at right.

Figure 7: Contributions of terrigenous and organic material to Cariaco sediment traps. Data shown are for Z trap (150 m, heavy line with symbols), A trap (250 m, thin black line), and C trap (880 m, grey line). Studied periods are highlighted with shading. Filled and open symbols show the fractional mass flux of terrigenous material and the total flux of organic carbon, respectively, in $\text{g}/\text{m}^2/\text{day}$ (<http://imars.marine.usf.edu/CAR/>).

Figure 8: Correlations between $\delta^{34}\text{S}$ values and concentrations of C_{20} thiophene, S^0 , and proto-kerogen S in Cariaco sediment traps. Symbols represent all available depths for five dates in winter 2007 (black triangles), October 2006 (open squares), February 2010 (open circles) and all other dates (Xs, for phytol thiophene only). Lines on the left-hand panels are linear regressions of winter 2007 data.

Figure 9: Comparison of water column-sourced abiotic OS and accumulated OS in Cariaco sediments. Sediment data (diamonds) are from ODP Core 1002B, collected at ~900 m water depth (Lyons et al., 2003; Werne et al., 2003). On the left panel, the open arrow indicates the average flux for samples plotting outside of the ‘S-addition’ field of Fig. 5; the black arrow is the average flux for C trap; both assume abiotic OS $\delta^{34}\text{S} = -30\text{‰}$. On the right panel, the open arrows indicate the bounding values used in the calculation in Table 4; the black arrow indicates the average $\delta^{34}\text{S}$ value of total proto-kerogen in C trap.

Table 1. Carbon and sulfur data for sinking particles

Table 2. Concentration and sulfur isotopic composition of extractable organic fractions and elemental sulfur in sinking particles

Table 3. Organosulfur compound concentrations and $\delta^{34}\text{S}$ values

Table 4: Estimated contribution of water column sulfurization to sedimentary proto-kerogen

Table 1	Date	Trap	Depth	Mass Flux	Proto-kerogen C		Proto-kerogen S		S:C
cup opened			m	g/m ² /d	mmol/m ² /d	δ ¹³ C (‰)	μmol/m ² /d	δ ³⁴ S (‰)	mol/mol
10/18/2006	Z	150		0.33	1.9	--	13	16.8	0.7%
	B	400		1.68	9.0	--	92	12.2	1.0%
	C	880		0.52	2.5	--	--	--	--
	D	1200		0.18	1.0	--	11	10.3	1.1%
2/10/2010	Z	150		0.67	4.0	--	58	17.4	1.4%
	A	225		0.66	7.3	-19.5	--	--	--
	B	400		1.91	16.1	-19.4	342	16.3	2.1%
	C	880		1.18	10.2	-19.4	259	14.3	2.5%
	D	1200		0.55	5.6	-19.3	114	14.6	2.1%
1/31/2007	B	400		0.58	3.8	-20.0	24	10.6	0.6%
	C	880		0.35	2.5	-19.5	35	9.3	1.4%
	D	1200		0.14	1.4	--	20	8.7	1.5%
2/14/2007	B	400		1.56	9.9	-19.5	284	11.8	2.9%
	C	880		1.12	8.5	-19.3	190	13.1	2.2%
	D	1200		0.72	5.5	-19.2	120	10.6	2.2%
2/28/2007	Z	150		0.52	2.3	--	31	12.8	1.3%
	B	400		0.71	3.6	-19.8	56	9.8	1.5%
	C	880		0.48	3.0	-19.5	46	10.3	1.5%
	D	1200		0.50	3.2	--	55	8.2	1.7%
3/14/2007	A	225		0.65	4.6	-18.5	173	15.4	3.7%
	B	400		0.36	2.6	-18.6	77	13.3	3.0%
	C	880		0.26	1.8	-18.9	68	8.8	3.8%
	D	1200		0.18	1.5	--	--	--	--
3/28/2007	B	400		2.08	10.6	-20.4	145	11.1	1.4%
	C	880		2.30	11.8	-20.0	188	9.0	1.6%
	D	1200		0.26	1.6	-20.4	24	11.0	1.5%
averages	A,Z	150-225		0.57	4.0	-19.01	69	15.6	1.8%
	B	400		1.27	7.9	-19.61	146	12.2	1.8%
	C	880		0.89	5.8	-19.43	131	10.8	2.2%
	D	1200		0.36	2.8	-19.62	57	10.6	1.7%
	all			0.79	5.2	-19.5	105	12.0	1.9%

Table 2

Date	Trap	Depth	Elemental S		Non-polar OS		Polar OS		Strongly polar OS	
cup opened		(m)	$\mu\text{mol}/\text{m}^2/\text{d}$	$\delta^{34}\text{S} (\text{‰})$	$\mu\text{mol}/\text{m}^2/\text{d}$	$\delta^{34}\text{S} (\text{‰})$	$\mu\text{mol}/\text{m}^2/\text{d}$	$\delta^{34}\text{S} (\text{‰})$	$\mu\text{mol}/\text{m}^2/\text{d}$	$\delta^{34}\text{S} (\text{‰})$
10/18/2006	Z	400	0.03	-5.2	0.03	10.8	0.33	4.3	0.10	8.2
	B	880	0.21	-8.1	0.32	5.2	1.60	5.0	0.37	8.5
	D	1200	0.01	-1.6	0.05	7.8	0.31	3.1	0.64	0.6
2/10/2010	Z	150	0.04	-5.2	0.02	8.9	0.62	14.8	0.18	13.7
	B	400	0.05	-8.1	0.03	10.4	1.99	12.1	0.71	12.4
	D	1200	0.16	-1.6	0.03	7.5	0.54	11.2	0.24	6.2
1/31/2007	B	400	0.07	--	0.02	--	0.57	1.8	--	--
	C	880	0.00	--	0.01	--	0.24	-2.6	--	--
	D	1200	0.00	--	0.01	--	0.09	3.8	--	--
2/14/2007	B	400	1.31	10.6	0.23	--	2.04	11.5	--	--
	C	880	1.70	10.8	0.13	--	1.83	16.8	--	--
	D	1200	1.51	4.6	0.06	--	1.21	10.4	--	--
2/28/2007	Z	150	--	9.7	0.18	5.9	1.56	5.1	0.16	5.9
	B	400	0.00	-4.4	0.08	9.7	1.13	4.0	0.53	13.6
	C	880	0.41	6.9	0.05	--	0.93	10.6	--	--
	D	1200	0.10	-3.9	0.02	8.6	0.94	6.2	0.59	9.6
3/14/2007	A	225	4.71	18.9	0.77	--	4.94	7.9	--	--
	B	400	--	--	0	--	--	--	--	--
	C	880	--	--	0	--	--	--	--	--
	D	1200	--	--	0	--	--	--	--	--
3/28/2007	B	400	0.17	-5.9	0.07	--	4.14	1.7	--	--
	C	880	4.62	0.0	0.18	--	6.75	10.0	--	--
	D	1200	0.00	--	0.02	--	0.19	2.9	--	--
averages	A,Z	150-225	1.60	4.5	0.25	8.5	1.86	8.0	0.15	9.3
	B	400	0.30	-3.2	0.13	8.4	1.91	6.0	0.54	11.5
	C	880	1.68	5.91	0.09	--	2.44	8.7	--	--
	D	1200	0.30	-0.6	0.03	7.9	0.55	6.3	0.49	5.5
	all		0.80	0.5	0.12	8.3	1.60	7.0	0.39	8.7

Table 3

Date **Trap** **Depth** **C₂₀ thiophene** **unidentified OSC (u-14)**

m nmol/g $\delta^{34}\text{S}$ (‰) nmol/g $\delta^{34}\text{S}$ (‰)

5/6/1999	B	400	0.01	--	0.12	--
	C	880	0.15	-21	0.11	--
11/18/1999	B	400	0.05	--	0.04	--
	C	880	0.22	--	0.04	--
	D	1200	0.16	-29.2	0.04	--
3/23/2000	B	400	0.38	-24.9	0.09	-23.2
	C	880	0.20	--	0.05	--
	D	1200	0.00	--	0.00	--
2/9/2001	B	400	0.28	-14.7	0.43	-9.8
	C	880	0.42	-17.4	0.00	--
	D	1200	0.16	-22.1	0.56	-8
8/30/2002	B	400	0.23	--	0.21	-30.5
	C	880	0.34	-18.2	0.21	-29.8
	D	1200	0.03	--	0.09	--
10/18/2006	B	400	0.27	-27.6	0.17	-28.1
	C	880	0.07	--	0.14	--
2/10/2010	B	400	0.14	-23.6	0.18	-22.3
	C	880	0.36	-27.1	0.27	-33
	D	1200	0.15	-29.9	0.20	--

Winter 2007:

1/31/2007	B	400	0.99	-11.7	--	--
	C	880	0.70	-12.5	--	--
	D	1200	0.28	-10.5	--	--
2/14/2007	B	400	1.04	-0.7	--	--
	C	880	1.09	-3.3	--	--
	D	1200	1.99	-7.6	--	--
2/28/2007	B	400	0.65	-11.9	--	--
	C	880	0.87	-7.4	--	--
	D	1200	0.55	-12.7	--	--
3/14/2007	A	225	1.25	3.1	--	--
	B	400	5.30	-2.5	0.62	--
	C	880	2.22	-13.7	0.00	--
	D	1200	2.03	-14.1	0.00	--
3/28/2007	B	400	1.12	-9.4	--	--
	C	880	2.93	-10.6	--	--
	D	1200	0.19	--	--	--

Table 4		ACCEPTED MANUSCRIPT						
Sample Group		n	Abiotic OS / Total OS			Equiv. sedimentary accumulation		
			%			μmol/g		
assumed abiotic OS $\delta^{34}\text{S}$:			(-30‰)	(-15‰)	(5‰)	(-30‰)	(-15‰)	(5‰)
All samples		23	14%	31%	48%	46	100	155
Figure 5 field								
'S-addition' field		6	13%	30%	46%	60	134	207
all other dates		17	15%	32%	50%	41	88	136
Trap depth								
Z/A (150 / 225 m)		4	11%	19%	37%	23	40	77
B (400 m)		7	13%	29%	45%	59	130	201
C (880 m)		6	16%	35%	55%	65	141	217
D (1200 m)		6	17%	37%	57%	30	65	100
Sedimentary OS (ODP Core 1002B)							μmol/g	
							95 – 136	
5 cm						126		
10 cm						95		
75 cm						124		
155 cm						136		

Figure 1

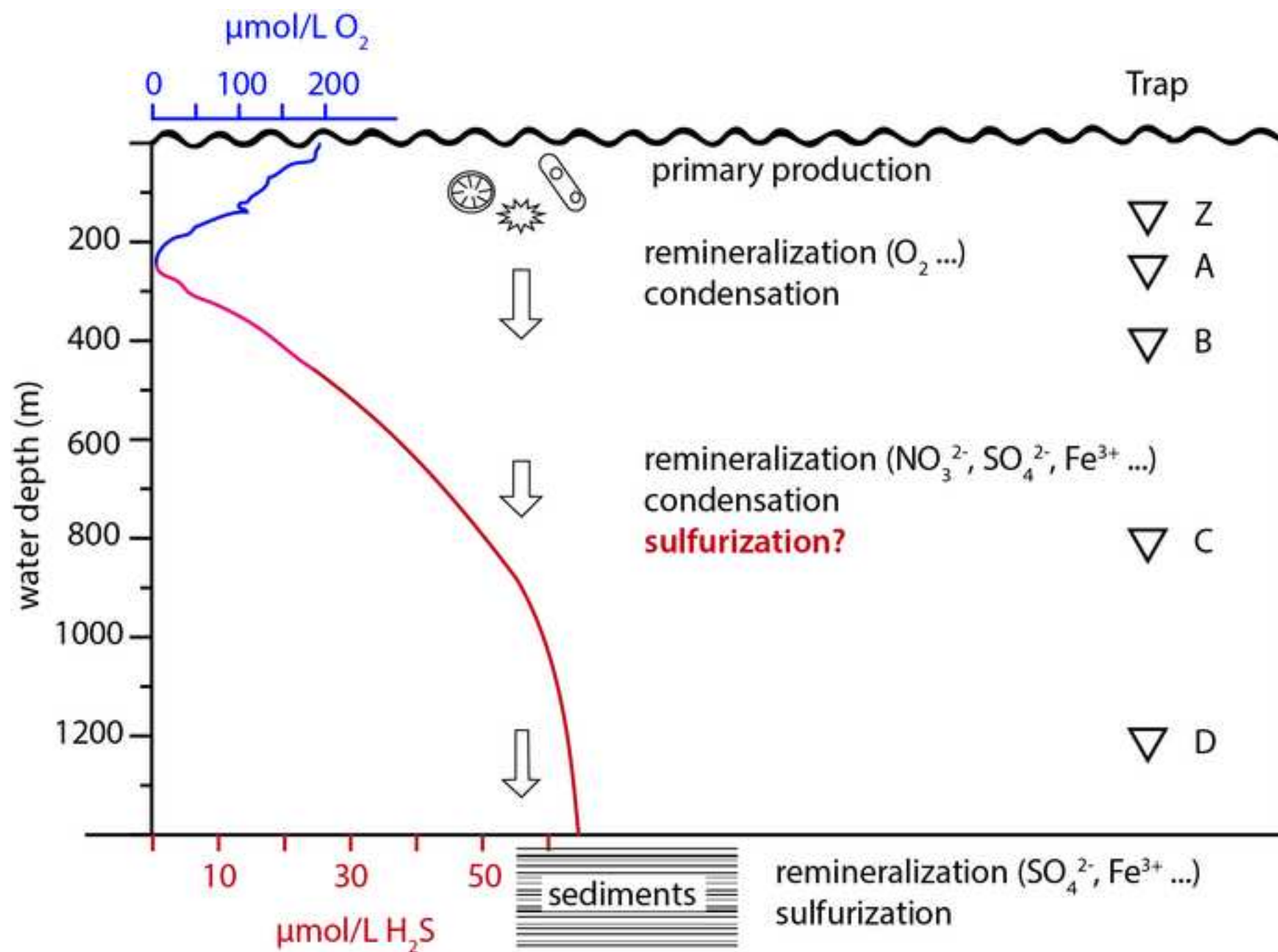


Figure 2

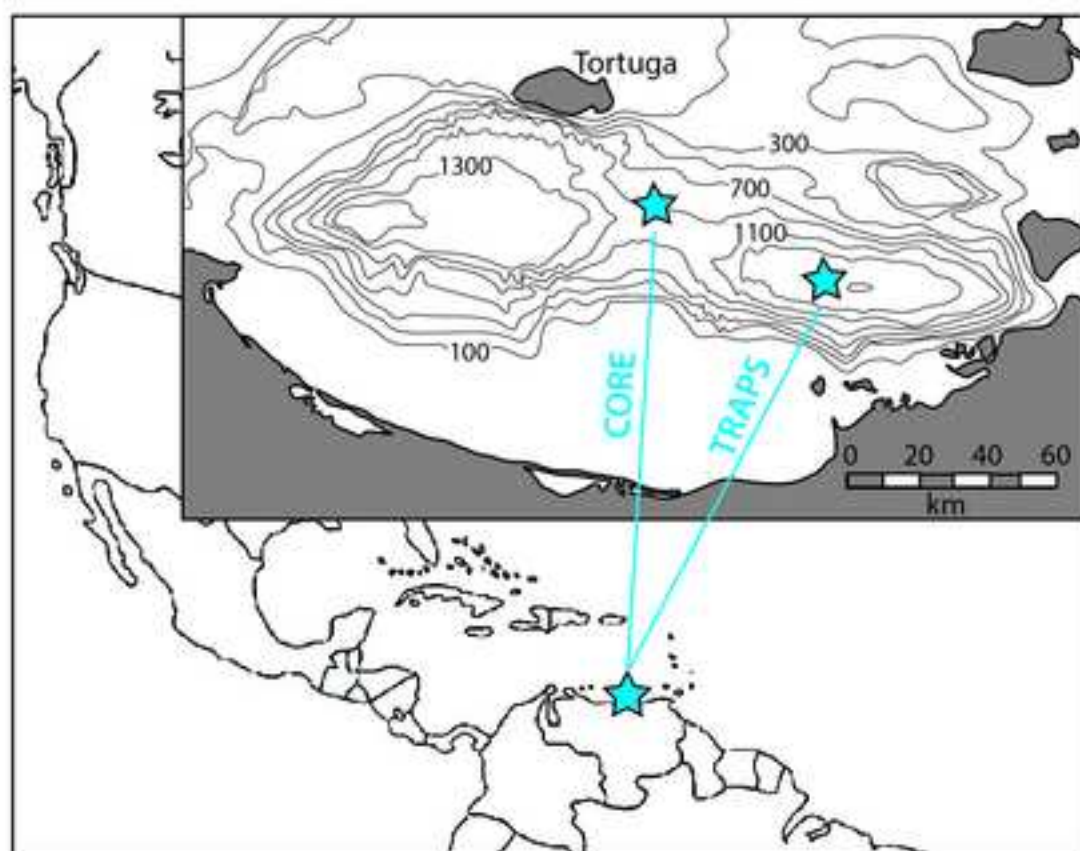


Figure 3

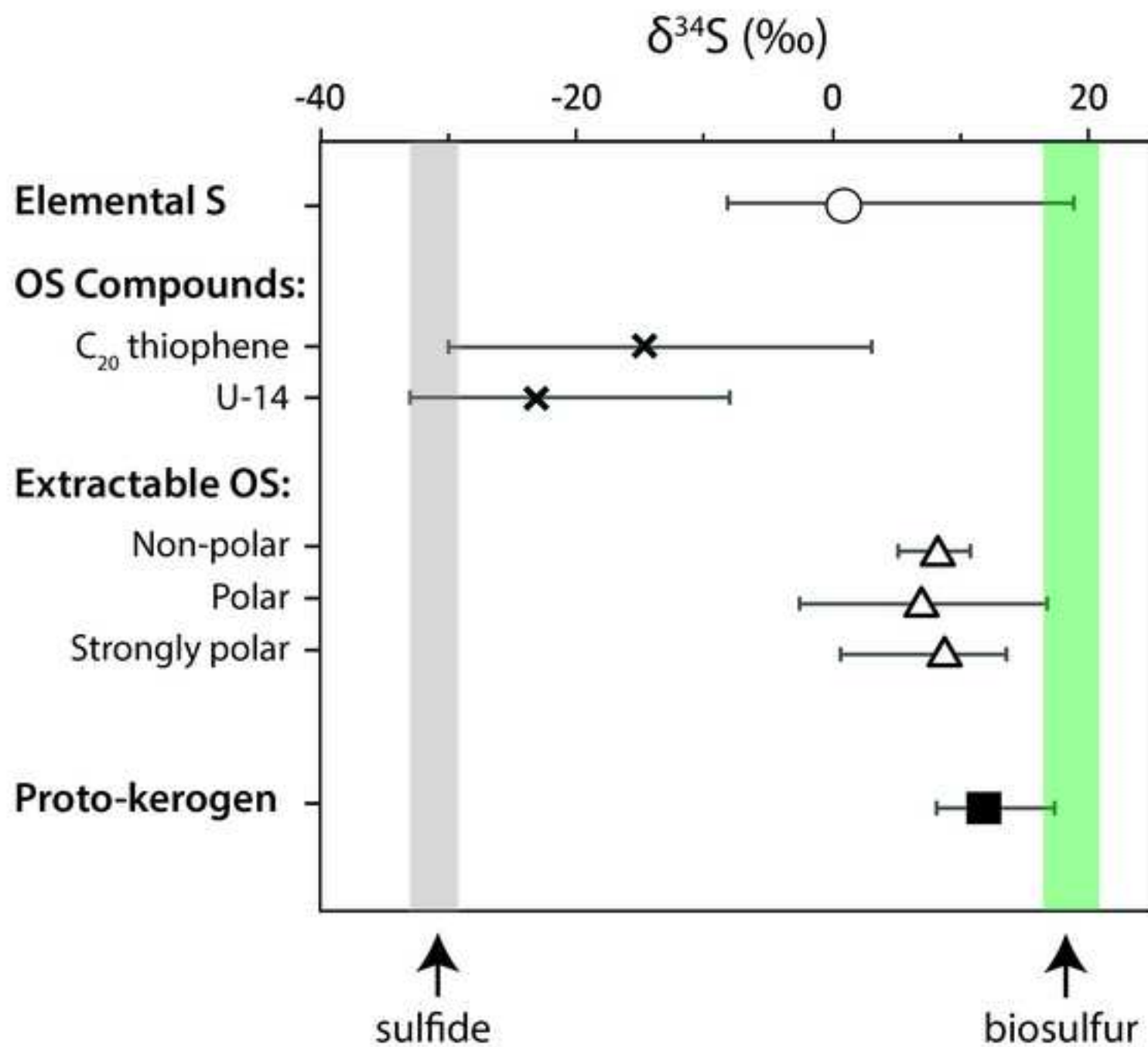


Figure 4

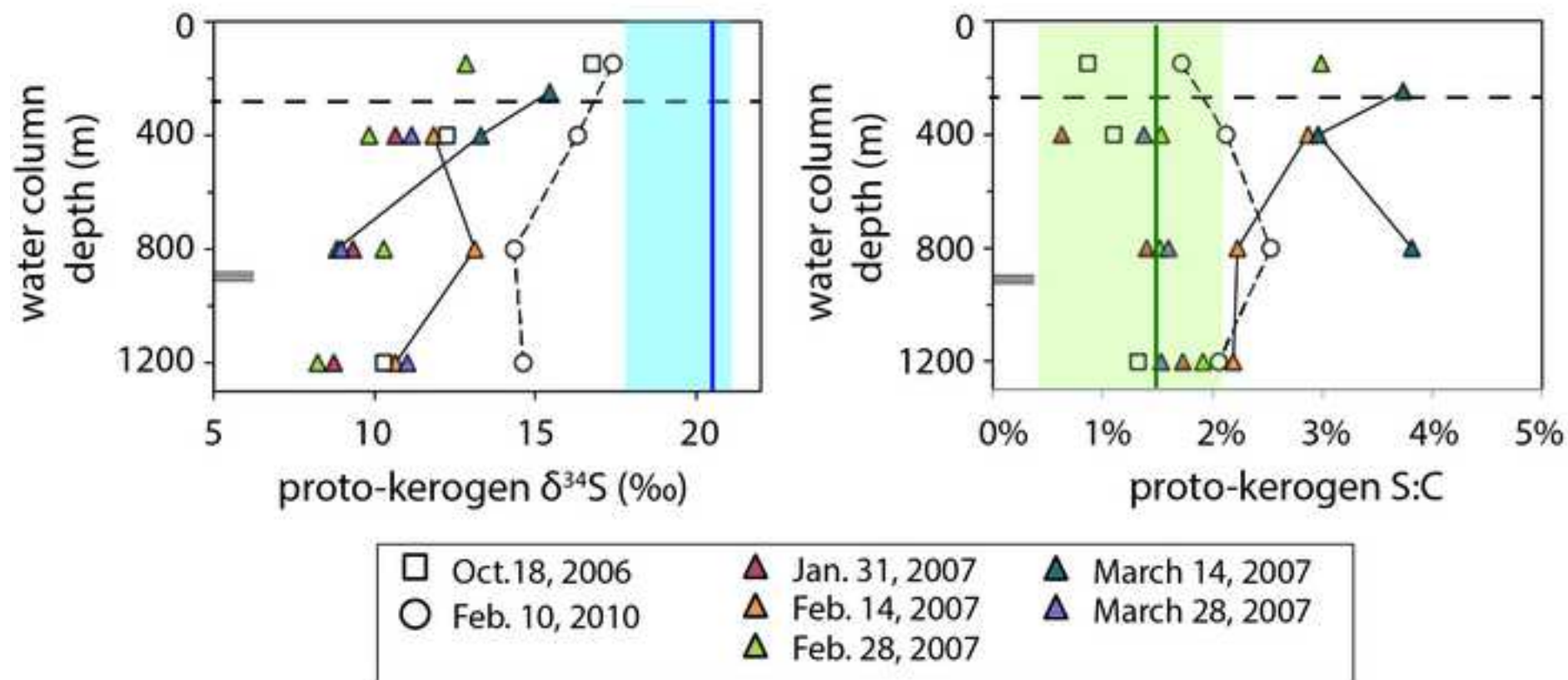


Figure 5

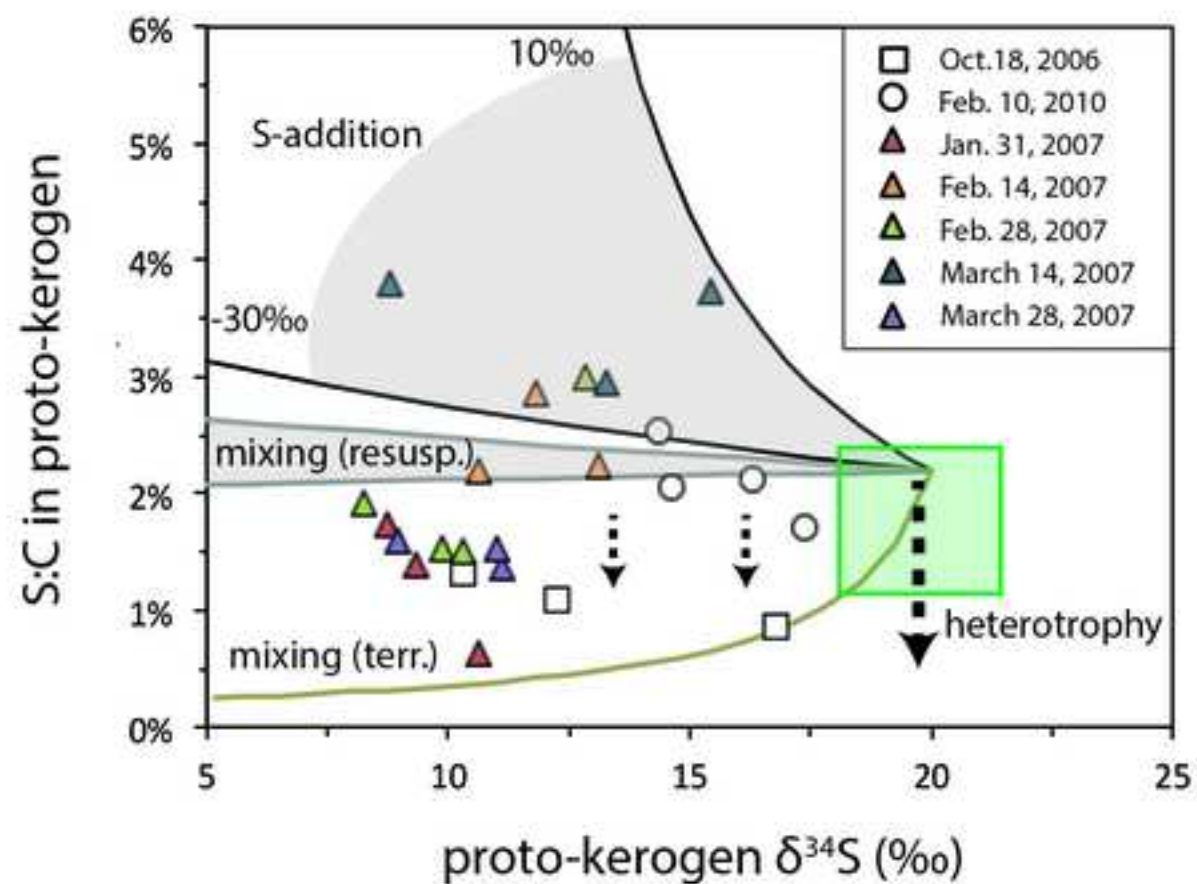


Figure 6

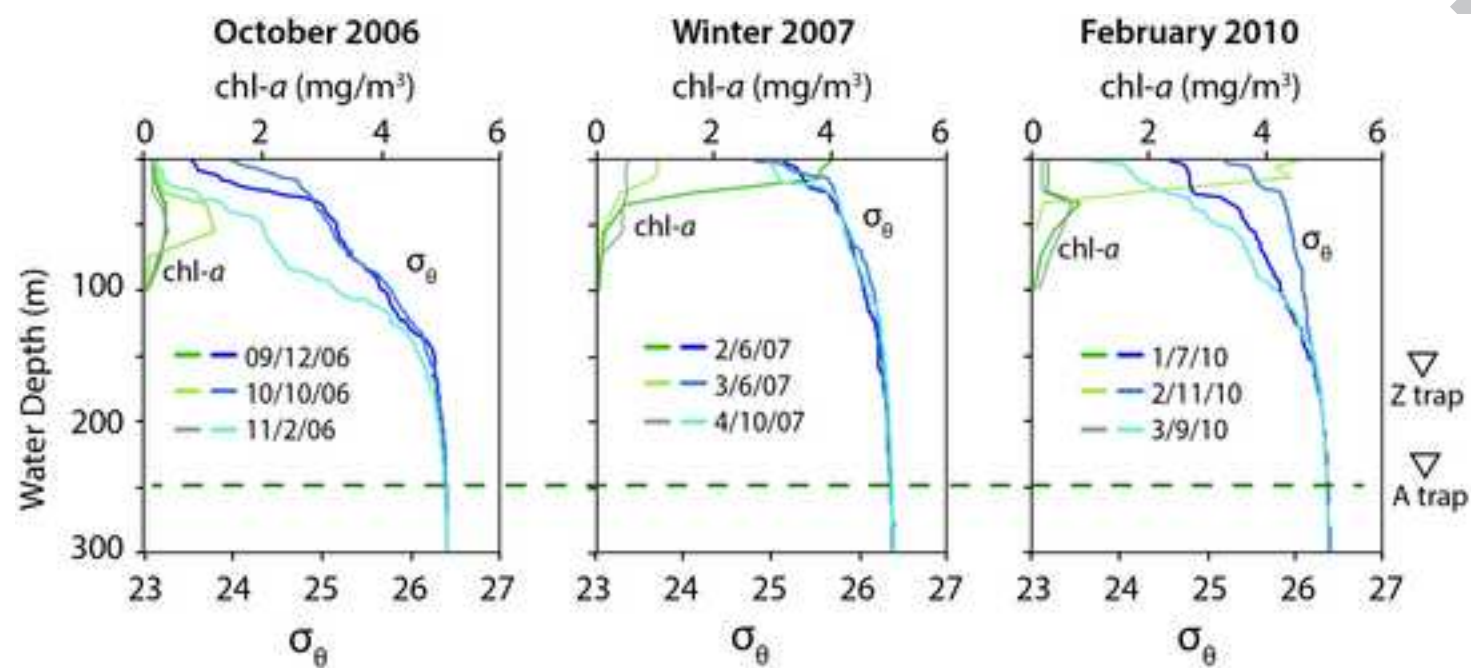


Figure 7

ACCEPTED MANUSCRIPT

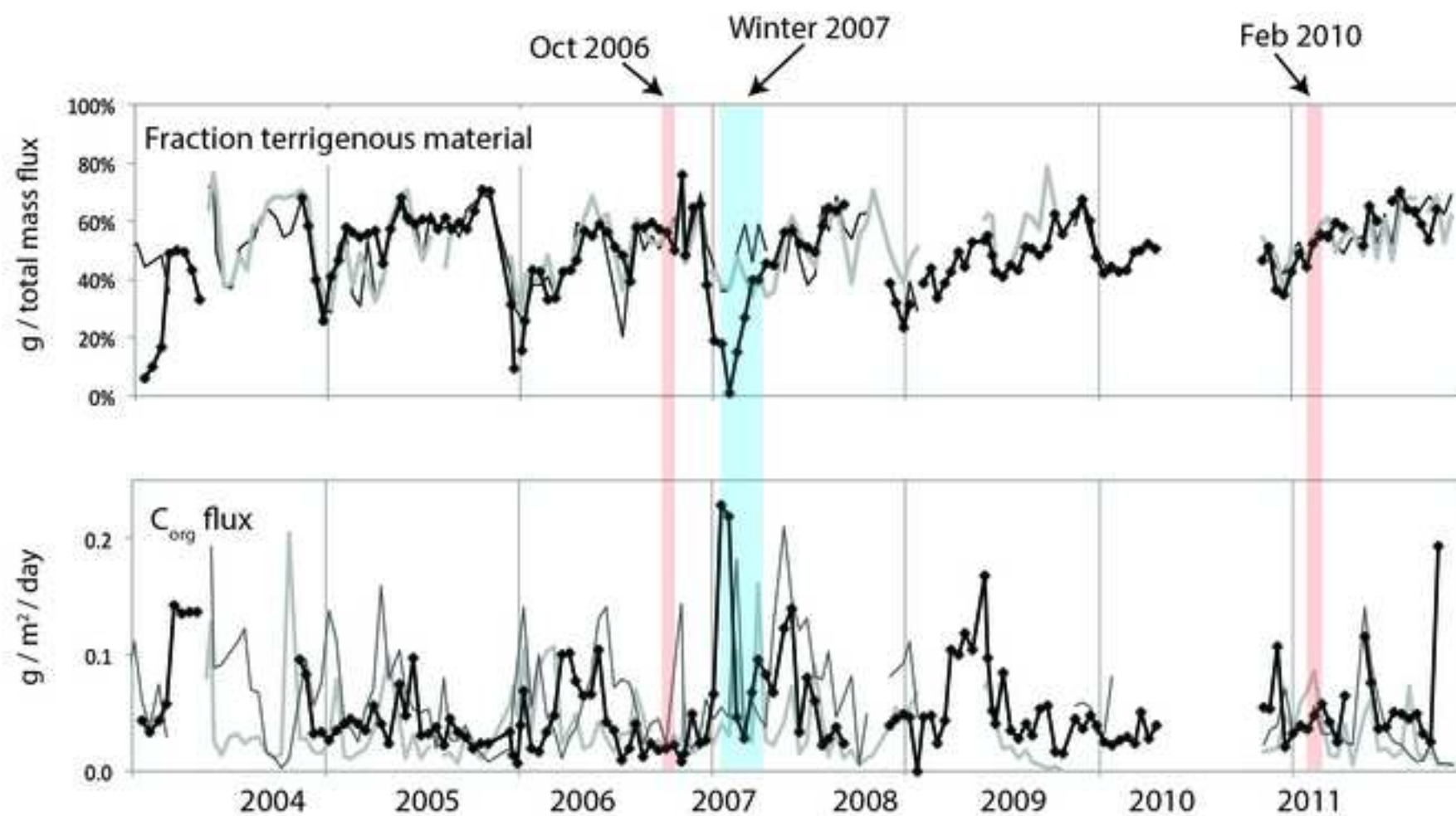


Figure 8

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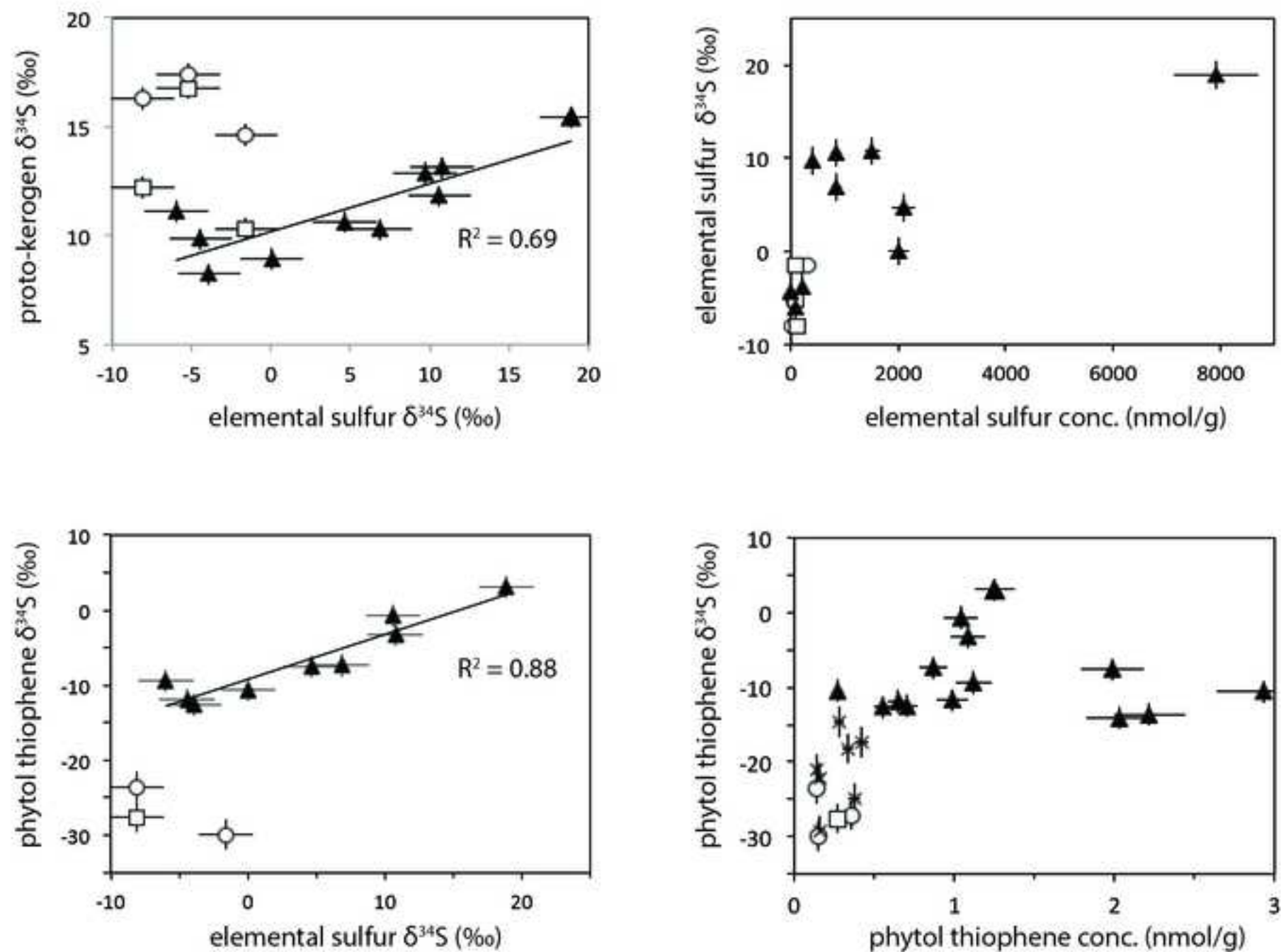


Figure 9

